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Adhesive Force of the Microstructures Measured by the Atomic Force Microscope

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Abstract

We propose a technique for the measurement of the work of adhesion of microstructures by using the atomic force microscope (AFM). The AFM system using a heterodyne interferometer has been developed to investigate the adhesive force acting between the sharp probe and the sample. The adhesive force acting on the probe is obtained from the deflection of the micromachined cantilever, which is measured precisely by the heterodyne interferometry. The sensitivity for the measurement of the adhesive force is evaluated to be 20pN.

The adhesive force was investigated by using the Si_3N_4 probe with the tip radius of 50*nm* and some kinds of materials used for micromachining process. When we use the SiO_2 substrate and five kinds of solution: (i)H_2O , (ii)C_2H_5OH , (iii)CH_3COCH_3 , (iv)CCl_4 and (v)KOH , the measured adhesive forces are in the range from 10 to 100nN. The adhesive force generated by CH_3COCH_3 is the smallest. This fact is consistent with the result that the rinse with CH_3COCH_3 reduces the pinning influence of the surface-micromachined structures. Moreover, the effect of the surface roughness and the contact area on the adhesive force are examined, and the results are discussed from a point of view of the macroscopic adhesive theory.

1 Introduction

Quantitative evaluation of the adhesive forces acting in microscopic region is important since the surface micromachined structures fabricated by Si unisotropic wet etching and by sacrificial layer etching are often plagued by the problem of adhering to the substrate. Moreover, the adhesive force as well as the frictional force often affects the movement of the microstructures having the contact sliding mechanism.

Recently several research groups have investigated the adhesion of the micromachined structures and proposed different mechanisms of the adhesion. Linder and de Rooij investigated the sticking of polysilicon microbeams fabricated by using silicon dioxide as a sacrificial layer and concluded that an electrostatic force caused the sticking(1). Alley et al. measured pull-off force by using micromachined test vehicles especially designed to evaluate the adhesion and proposed that the adhesive bond by silica residues was responsible for the adhesion(2). Mastrangelo and Hsu presented a simple experimental technique for the measurement of the adhesion of microstructures(3). The cantilever arrays having different length and thickness were fabricated, and the adhesion was investigated from the detachment length of the cantilever. The value of surface energy were found to be $140mJm^{-2}$ for the combination of polysilicone beam and a silicon substrate. The surface energy of the hydrophilic Si substrate was not different considerably from that of the hydrophobic Si substrate. Scheeper et al. investigated the attractive forces between PECVD silicon nitride cantilever array and oxidized silicon substrate and it was concluded that the sticking of the cantilevers was due to the adsorption of the water molecules(4). However, the nature and the magnitude of the adhesive forces are not understood in detail so far.

On the other hand, recently the atomic force microscope (AFM), which detects the interaction force in a very week force range, has proved to be a powerful tool in imaging nonconductive surface with a high lateral resolution(5). The attractive interactions between the AFM probe and surface include van der Waals force, electrostatic force, capillary force of liquids present in the gap between the probe and sample. Under the appropriate conditions, the respective forces can be evaluated by AFM with the resolution surpassing that of currently available techniques. In the basic researches of tip-sample interactions and in some practical applications, there is also a high level of interest in adhesion measurement using AFM(6)(7)(8).

In this paper, we propose a technique for the measurement of the work of the adhesive force acting on microstructures. A high resolution AFM system using a laser heterodyne interferometry is constructed to measure the absolute value of the adhesive force. The adhesive forces acting between Si_3N_4 probe and Si and SiO_2 substrates are mea-

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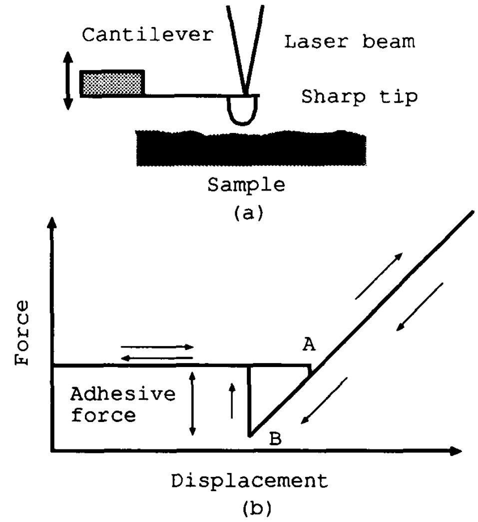

Fig. 1: (a) Schematic diagram of the measurement principle and (b)schematic diagram of the force curve.

sured after the substrates are immersed in several kinds of etch and rinse solutions. The adhesive force acting on AFM probe is also evaluated theoretically. The influences of humidity and temperature on the adhesion are examined. Since the surface roughness is measured by AFM, the relation between the surface roughness and the adhesive force is also investigated. Moreover, the adhesive force by the solid bridging between the micromachined SiO_2 cantilever and Si surface is estimated by pulling it with AFM probe.

2 Measurement principle and attractive forces

In order to examine the properties of the adhesion in micromechanical system, the simple structures such as cantilever and bridge were previously used in the experiments(2)(3)(4). These experimental configurations are similar to the force sensor of the AFM system. Figure 1(a) shows the principle of the measurement by using the AFM. In the force microscope, the force acting on the probe is measured preciously from the deflection of the probe(5)(7). The probe of the force microscope consists of the sharp tip and the cantilever having a low spring constant. The motion of the tip can be monitored as a function of the sample translation. From the deflection of the cantilever, the force acting between the tip and sample surface is obtained. In the case of the adhesion measurement, adhesive force is obtained from the transition of the force curve(8).

Figure 1(b) shows the schematic diagram of the force curve (absolute force versus sample displacement) obtained by the AFM. The vertical and horizontal axes denote the force acting on the sample and the sample displacement, respectively. When the AFM probe approaches the sample, a sudden attractive force is exerted on the probe (point A). From the transition, it is possible to estimate the thickness of the adsorbed liquid layer. As the sample stage moves closer, the force changes from attractive to repulsive. In the repulsive region, the distance between the probe and the sample is very small and the probe is considered to be in contact with the sample surface. When the sample, which is in contact with the sample surface, moves toward the probe, the probe deflection increases linearly as a function of sample displacement. Retracting the probe, the repulsive force decreases. When the probe is peeled from the sample surface, the force decreases until a minimum is obtained. On further withdrawal, the pull-off force overcomes the adhesive force and the probe separates from the surface. The maximum value of the attractive force is determined from the transition (point B) as shown in Fig. 1(b).

These are four attractive forces acting on the tip, which are van der Waals force, electrostatic force, capillary force, and the force by solid bridging. The van der Waals forces (F_{vdw}) acting between a sphere and flat substrate result from the interaction between the instantaneous dipole moments of atoms(2)(9)(10). The force is given theoretically by

$$F_{vdw} = -\frac{AS}{6\pi d^3}. \tag{1}$$

Here, A represents the Hamaker constant. S and d represent the shared area and the separation of the parallel surfaces. When microelectromechanical systems are fabricated by the wet etching of sacrificial layers, dimensions of them are usually in the micrometer range, and the separations of the micromachined parts are in the submicrometer range. F_{vdw} of two flat Si surface is calculated, by using the values of $A = 1.7eV, S = 10nm^2$ and $d = 10nm$, to be $0.1pN$.

Electrostatic force (F_{ef}) may arise because of the electrostatic charging or the differences in the work functions of the opposed surfaces(2)(10). The force is given by

$$F_{ef} = -\frac{\epsilon_0 U^2 S}{2d^2}. \tag{2}$$

Where, U represents the potential difference. ϵ_0 denotes the permittivity. Assuming that the surface is not charged, the difference of the work function U is of the order of $1V$ and $S = 10nm^2$, F_{ef} is smaller than $1pN$, in the case of $d < 10nm$.

In the recent studies of AFM, it is pointed out that the surface is covered by the water molecules condensed on the surface under the atmospheric environments(6). In the case, capillary force is generated when the two surfaces are located at the very close separation. The capillary force is an effect of the surface tension of the condensed liquids that

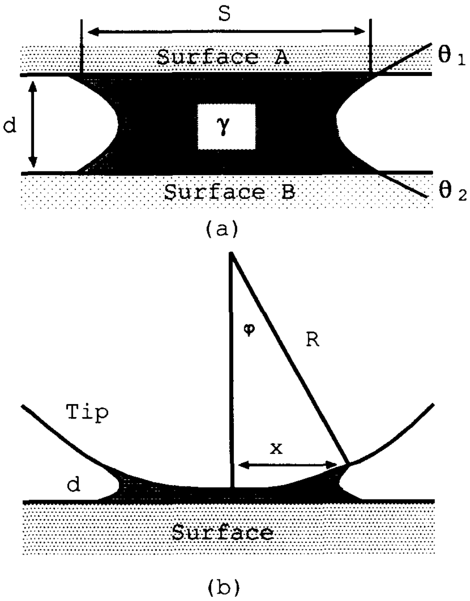

Fig. 2: Models of the liquid capillary.

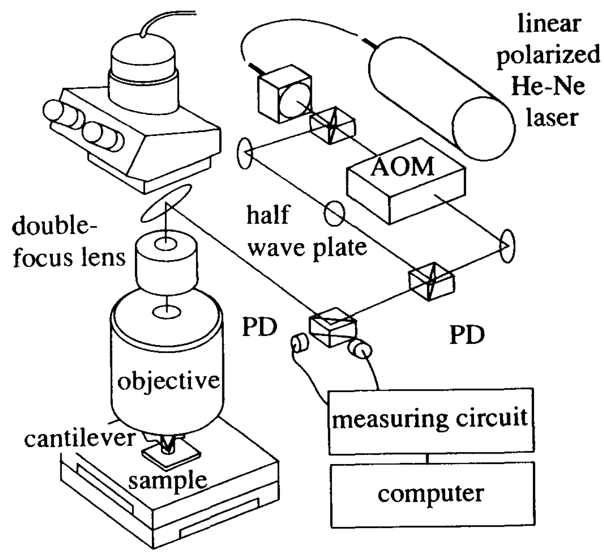

Fig. 3: Schematic diagram of the developed atomic force microscope.

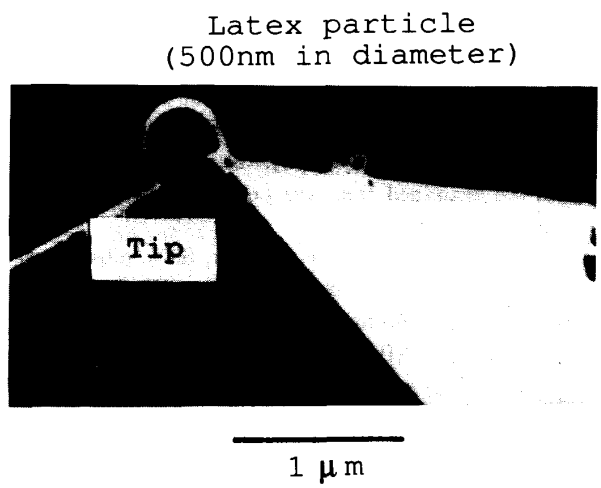

Fig. 4: Photograph of the tip by SEM.

are trapped between a small gap of the probe and the sample (Fig. 2(a)). Under the conditions shown by Fig.2(a), the capillary force is calculated by the equation(2)(10),

$$F_{cf} = -\frac{\gamma(\cos\theta_1 + \cos\theta_2)S}{d}, \tag{3}$$

where θ_1 and θ_2 are the contact angles between the condensed liquid surface and the two solid surfaces, which approach 0° for hydroxylated chemical oxide surface. The symbols γ and S are the surface tension and the shared area of the parallel surfaces. Assuming that the contact angles are small ($\theta_1 \simeq \theta_2 \simeq 0$), and the separation d can be negligible as compared with the radius R of the tip (Fig.2(b)), Eq. (3) is simplified to be

$$F_{cf} = -4\pi\gamma R. \tag{4}$$

Here the cross section S is replaced by $S = \pi x^2 \simeq 2\pi Rd$.

The capillary force was calculated to be of the order from 10^{-7} to 10^{-8}N under the conditions that the separation was in the range of one micrometer or submicrometer. Therefore, the capillary force is considered to be predominant under the condition that the surface is covered by the liquid layer.

On the other hand, the solid bridging is caused by the impurities which are introduced in the liquid through dissolution of the particle or substrate materials(2). The adhesive force resulting from solid bridging is difficult to estimate because of the variability in the wet etching process. In order to evaluate typical value of the adhesive force due to the solid bridging, we measured the force to peel the pinned cantilevers by the probe of the AFM.

3 Experimental setup

Figure 3 shows the schematic diagram of the experimental system(11). The V-shaped cantilever made of Si_3N_4 (Park Scientific Instruments) is used as a probe. The dimensions of the cantilever are $200\mu m$ long, $36\mu m$ wide and $0.6\mu m$ thick and the spring constant of the probe is $0.064N/m$. A sharp small tip is fabricated at the edge of the probe. The top radius of the tip is estimated to be less than $50nm$ from an observation by using an scanning electron microscopy (SEM). The SEM photograph of the tip is shown in Fig. 4. The sphere shown in this figure is a latex particle with 500nm diameter. The adhesive force acting between the

Si_3N_4 surface and the sample surface is measured by using the probe.

The deflection of the cantilever is measured by a heterodyne interferometry using doubled focused lens as beam splitter and recombiner. A He-Ne laser is used as a light source of the interferometer as shown in Fig. 3. The incident beam are divided into the signal beam and the reference beam. The signal beam is focused on the rear surface of the probe and the phase difference between the reflected signal beam and the reference beam is detected. The resolution corresponding to the probe deflection is 0.3 nm.

A sample mounted on a stage is moved to x, y and z directions independently by three piezo electric actuators. In order to avoid the hysteresis of the piezoelectric actuators, the displacement as a function of the voltage applied to the piezoelectric actuators was measured and the controlled voltage that was subject to obtain the linear movement of the stage was determined. By this method, we obtained the excellent linearity less than 1% for the stage movement.

The force acting on the probe is determined from the deflection of the micromachined probe (cantilever and tip), since the force is proportional to the deflection of the cantilever. The sensitivity for the measurement of the probe deflection is $0.3nm$, and thus, that for the applied force is approximately $20pN$. Since the AFM can also be used to image the sample topography, the properties of the adhesion are examined from the point of view of the surface roughness.

In the experiments, the Si wafer, SiO_2 substrate, SiO_2 frosted glass were used as samples. The samples were immersed into the five kinds of liquid. The liquids were CH_3COCH_3 , C_2H_5OH , CCl_4 , KOH and H_2O , which were frequently used in the etch and rinse processes. After taking out the samples from the liquids, they were heated at 50 °C for 5 minutes. The same kinds of sample that were dried in air were also used in the experiments. The force curves were measured by changing the sample temperature and the humidity in air. The sample having different roughness was also tested in the experiment.

4 Results of the capillary force measurements

Figure 5 shows the typical force curve obtained by using SiO_2 sample and KOH solution under the condition that the temperature is 22°C and the humidity is 40%. This sample is not dried and we believe there are thick KOH layer on the surface. As shown in Fig. 5, two transitions of the force curve are obtained. From the first transition (point A) shown in Fig. 5, the thickness of the liquid layer is estimated roughly to be $0.1\mu m$. The first transition does not always appear clearly in the measured force curves.

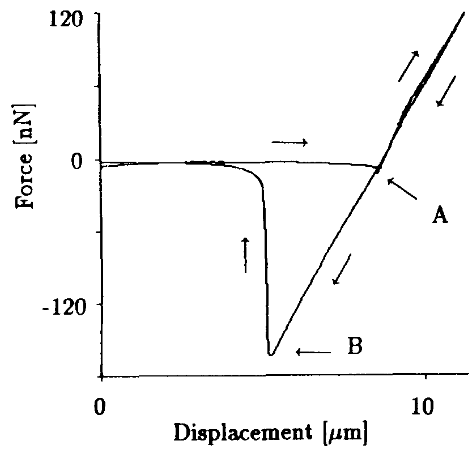

Fig. 5: Typical force curve obtained by using SiO_2 sample and KOH solution without heating process. The temperature is 22°C and the humidity is 40%.

The second transition (point B) appears obviously as shown in Fig. 5. From the value of the transition, the maximum adhesive force is calculated. Since the transition occurs at the critical point of the force equilibrium, the measured adhesive force is scattered somewhat. We repeated the measurement of force curve more than 50 times, and the average values are obtained. The uncertainty of the adhesive force evaluated from the scatter of the measured values is typically less than 20 %.

The surface topographies obtained by the developed AFM are shown in Fig. 6. The surface of the smooth SiO_2 substrate is imaged in Fig. 6(a). The imaged area is $100 \times 100nm^2$. The surface roughness is evaluated approximately to be less than $1nm$. The surface of the rough SiO_2 substrate is imaged in Fig. 6(b). The imaged area is $10 \times 10\mu m^2$. The surface roughness is evaluated to be approximately $1\mu m$. We also measured the Si substrate used in the experiments. The roughness of the Si surface was less than $1nm$.

A part of the results of the adhesive force measurements is shown in Table 1. In this case, we used the smooth SiO_2 substrate and five solutions. The surface roughness of the SiO_2 substrate is evaluated to be approximately $1nm$. The temperature and the relative humidity are 23 $°C$ and 26 %. The theoretical values are obtained by using Eq. (4), assuming the radius of the tip is $50nm$. The adhesive forces generated by CH_3COCH_3 and C_2H_5OH are smaller than the other solutions. The experimental results shown in Table 1 are explained well with the theoretical calculations.

Table 2 shows another set of the experimental results obtained for the smooth SiO_2 substrate. The temperature and the relative humidity are 21°C and 61%. In the case of higher humidity, the values of the adhesive force are

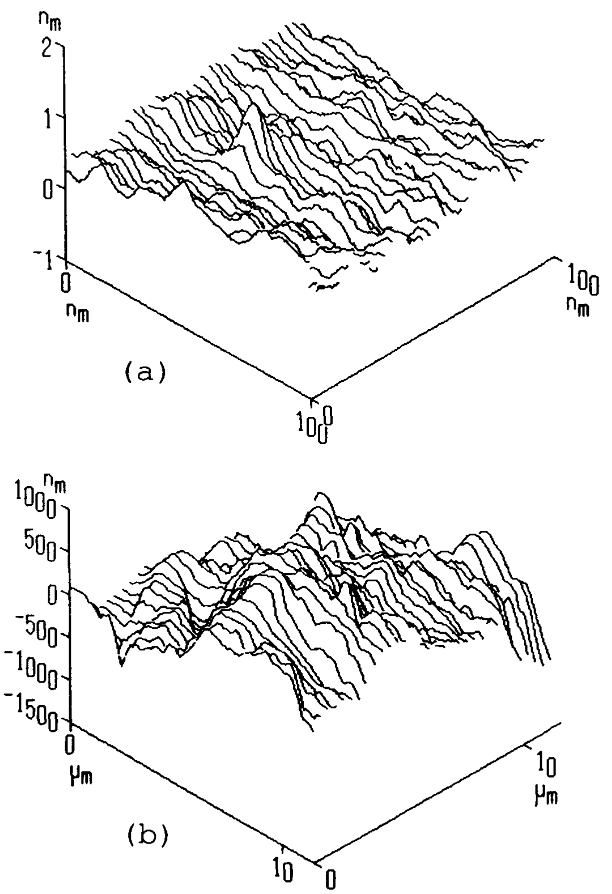

Fig. 6: The surface topography of the (a) smooth SiO_2 substrate and (b) frosted SiO_2 substrate.

Liquid	Experimental [nN]	Theoretical [nN]
H_2O	45.1	45.7
CH_3COCH_3	13.5	14.8
C_2H_5OH	12.4	13.8
KOH	26.8	
CCl_4	32.2	16.7

Table 1: The adhesive forces measured for the different solutions by using Si_3N_4 tip and smooth SiO_2 substrate. The temperature and the relative humidity are 23°C and 26%.

higher than those shown in Table 1. In this case, there were thicker liquid layers on the sample surface, and thus, the adhesive forces increased. In the case of higher humidity, it is believed that the water molecule in the air influences the thickness of the liquid layer considerably. The results shown in Tables 1 and 2 agree with the fact that the rinse with CH_3COCH_3 or C_2H_5OH reduces the pinning effect of

Liquid	Adhesive Force [nN]
H_2O	74.8
CH_3COCH_3	21.3
C_2H_5OH	24.8
KOH	34.8
CCl_4	74.4

Table 2: The adhesive forces measured for the different solutions by using Si_3N_4 tip and smooth SiO_2 substrate. The temperature and the relative humidity of the experimental system are 21°C and 61%.

the surface-micromachined structures.

In order to examine the influence of the surface roughness on the adhesive force, the force curves were also obtained by using the frosted SiO_2 substrate, whose surface roughness was $1\mu m$. The value of the adhesive force for H_2O was obtained to be approximately $18.6nN$ in air. The temperature and the relative humidity were 21°C and 51%. The force curves were obtained under the same conditions with the smooth SiO_2 substrate. The surface roughness of the smooth SiO_2 substrate was approximately $1nm$. The value of the adhesive force was $48.5nN$. This result indicated that the surface roughness decreased the adhesive force.

We carried out the similar experiments to measure the attractive force between the Si_3N_4 probe and the silicon wafer. The roughness of the Si surface was evaluated less than $1nm$. The temperature and the relative humidity were 17°C and 43%. The samples were immersed in the H_2O liquid and dried in air. The value of the adhesive force was $28.7nN$. The value for the smooth SiO_2 substrate under the same conditions was also measured to be $27.0nN$. This result can be explained by the fact that the surface of the Si substrate is oxidized naturally under atmospheric environment.

The adhesive force was evaluated to be of the order of $10^{-8}N$ by the experiments described above. In these experiments, the shared contact area is of the order of $100nm^2$. Assuming that the adhesive force is proportional to the contact area as shown Eq. (3) and the contact area in the micromachined parts is $10\mu m^2$, the adhesive force acting on the micromachined parts is estimated to be of the order of one millinewton or more.

5 Adhesive force by solid bridging

In order to evaluate the adhesive force by solid bridging, we have carried out the experiment to peel the micromachined cantilever which is pinned to the substrate after rinse process. Figure 7 shows the schematic diagram of the experiment. Using the probe of the AFM, the pinned cantilever was pulled upward. The spring constant of the

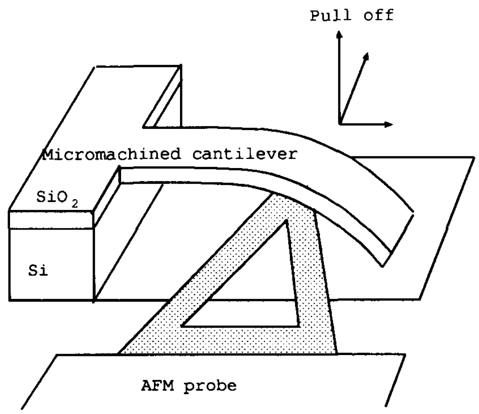

Fig. 7: Schematic diagram of the pinned cantilever and AFM probe. The AFM probe moves upward and pulls the pinned cantilever up.

AFM probe used in this experiment was $0.32N/m$. The sample cantilever was made of the thermally oxidized SiO_2 film on the Si substrate and the Si substrate was etched anisotropically by KOH solution. The dimensions of the cantilever was $150\mu m$ long, $20\mu m$ wide and approximately $0.5\mu m$ thick. The free end of the cantilever is attached to the Si surface by the solid bridging. The area of the solid bridging was evaluated to be $10\mu m \times 20\mu m$ by the observation with optical microscope.

Increasing the force up to $1\mu N$ by pulling with AFM probe, the sample cantilever was not released. Therefore in the case of this sample, the adhesive force was considerably strong. Although the solid bridging is dependent on the etch and rinse process, the adhesive force by the solid bridging seems to be strong, compared with the capillary force. Selecting the stiffness of the cantilever, the AFM is also a novel tool to palpate the micromachined structure.

6 Summary

We investigated the adhesive force acting between the Si_3N_4 probe (top radius of $50nm$) and the some kinds of flat substrate immersed into the etch and rinse solutions. Adhesive forces were measured from the transition of the force curve. When we used the SiO_2 substrate and five kinds of solution: (i)H_2O , (ii)C_2H_5OH , (iii)CH_3COCH_3 , (iv)CCl_4 and (v)KOH , the measured adhesive forces were in the range from 10 to $120nN$. The adhesive forces generated by CH_3COCH_3 and C_2H_5OH were smaller than others. This fact is consistent with the result that the rinse with CH_3COCH_3 and C_2H_5OH reduces the pinning effect of the surface-micromachined structures. The force acting on the microscopic region was discussed theoretically. The calculated capillary force agreed well with the experimental results when the humidity of the surrounding air is low. Therefore, in the case of low humidity, the adhesive force was explained by the surface tension of the solution covering the sample substrate.

The measured adhesive force increased with the increase of the humidity. in the surrounding air. The surface roughness was also measured by the AFM and the influence of the surface roughness on the adhesive force was examined. It was shown that the adhesive force acting on the rough surface was lower than that acting on the smooth surface. Since the rough surface made the effective surface separation large, the adhesive force decreased. Moreover, the adhesivex force by solid bridging was tested by the palpation with AFM probe.

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